PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09K 5/04	A1	(11) International Publication Number: WO 97/07179 (43) International Publication Date: 27 February 1997 (27.02.97)

(21) International Application Number: PCT/GB96/01955

(22) International Filing Date: 12 August 1996 (12.08.96)

(30) Priority Data:
9516920.7 18 August 1995 (18.08.95) GB

(71) Applicant (*for all designated States except US*): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): POWELL, Richard, Llewellyn [GB/GB]; 9 Sadler's Wells, Bunbury, Tarporley, Cheshire CW6 9NV (GB). CORR, Stuart [GB/GB]; 31 Foxhills Close, Appleton, Cheshire WA4 5DH (GB). MURPHY, Frederick, Thomas [GB/GB]; 53 Fairways, Frodsham, Cheshire WA6 7RY (GB). MORRISON, James, David [GB/GB]; 39 Sandown Crescent, Cuddington, Northwich, Cheshire CW8 2QN (GB).

(74) Agents: DEE, Ian, Mark et al.; ICI Chemicals & Polymers Limited, Intellectual Property Dept., P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).

(81) Designated States: AU, BR, CA, CN, JP, KR, MX, NO, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: REFRIGERANT COMPOSITIONS

(57) Abstract

A non-azeotropic refrigerant composition is described comprising (A) carbon dioxide (CO_2), (B) pentafluoroethane (R-125), and (C) 1,1,1-trifluoroethane (R-143a).

REFRIGERANT COMPOSITIONS

The present invention relates to non-azeotropic refrigerant compositions and more particularly to non-azeotropic refrigerant compositions which can be used in the low temperature refrigeration applications currently satisfied by refrigerant R-502 which is an azeotropic mixture of chlorodifluoromethane (refrigerant R-22) and chloropentafluoroethane (refrigerant R-115).

Heat transfer devices of the mechanical compression type such as refrigerators, freezers, heat pumps and air conditioning systems are well known. In such devices a refrigerant liquid of a suitable boiling point evaporates at low pressure taking heat from a surrounding heat transfer fluid. The resulting vapour is then compressed and passes to a condenser where it condenses and gives off heat to another heat transfer fluid. The condensate is then returned through an expansion valve to the evaporator so completing the cycle. The mechanical energy required for compressing the vapour and pumping the liquid may be provided by an electric motor or an internal combustion engine.

In addition to having a suitable boiling point and a high latent heat of vaporisation, the properties preferred of a refrigerant include low toxicity, non-flammability, non-corrosivity, high stability and freedom from objectionable odour.

Hitherto, heat transfer devices have tended to use fully and partially halogenated chlorofluorocarbon refrigerants such as trichlorofluoromethane (refrigerant R-11), dichlorodifluoromethane (refrigerant R-12), chlorodifluoromethane (refrigerant R-22) and the azeotropic mixture of chlorodifluoromethane and chloropentafluoroethane (refrigerant R-115); the azeotrope being refrigerant R-502. Refrigerant R-502, for example, has been widely used in low temperature refrigeration applications.

However, the fully and partially halogenated chlorofluorocarbons have been implicated in the destruction of the earth's protective ozone layer and as a result the use and production thereof has been limited by international agreement.

Whilst heat transfer devices of the type to which the present invention relates are essentially closed systems, loss of refrigerant

to the atmosphere can occur due to leakage during operation of the equipment or during maintenance procedures. It is important, therefore, to replace fully and partially halogenated chlorofluorocarbon refrigerants by materials having low or zero ozone depletion potentials.

In addition to the possibility of ozone depletion, it has been suggested that significant concentrations of chlorofluorocarbon refrigerants in the atmosphere might contribute to global warming (the so-called greenhouse effect). It is desirable, therefore, to use refrigerants which have relatively short atmospheric lifetimes as a result of their ability to react with other atmospheric constituents such as hydroxyl radicals.

Replacements for some of the chlorofluorocarbon refrigerants presently in use have already been developed. These replacement refrigerants tend to comprise selected hydrofluoroalkanes, i.e. compounds which contain only carbon, hydrogen and fluorine atoms in their structure. Thus, refrigerant R-12 is generally being replaced by 1,1,1,2-tetrafluoroethane (R-134a).

Although suitable replacement refrigerants are available, there is always a need for new refrigerants having a low or zero ozone depletion potential that are capable of replacing the chlorofluorocarbon refrigerants presently in use such as R-502. Furthermore, very real benefits could be realised by a new replacement refrigerant having a higher refrigeration capacity than the replacement refrigerants known in the art.

The present invention provides a non-azeotropic refrigerant composition comprising a mixture of compounds having low or zero ozone depletion potentials which can be used in the low temperature refrigeration applications currently satisfied by refrigerant R-502. The non-azeotropic refrigerant composition of the invention can exhibit an advantageously high refrigeration capacity.

According to the present invention there is provided a non-azeotropic (zeotropic) refrigerant composition comprising:

(A) carbon dioxide (CO_2);

(B) pentafluoroethane (R-125); and

(C) 1,1,1-trifluoroethane (R-143a).

The zeotropic refrigerant composition of the invention comprises three separate components.

The first component (component (A)) is carbon dioxide (CO_2) which exhibits a low temperature refrigeration action subliming at around -78.5°C. The second component (component (B)) is pentafluoroethane (R-125) which has a boiling point of around -48.5°C. The third component (component (C)) is 1,1,1-trifluoroethane (R-143a) which has a boiling point of around -47.6°C.

The refrigerant composition of the invention may also contain 1,1,1,2-tetrafluoroethane (R-134a) which has a boiling point of around -26.5°C.

The amounts of the CO_2, R-125 and R-143a and the amount of the R-134a (if included) in the refrigerant composition may be varied within wide limits, but typically the refrigerant composition will comprise from 1 to 20 % by weight CO_2, from 25 to 70 % by weight R-125, from 25 to 70 % by weight R-143a and from 0 to 25 % by weight (for example, from 1 to 25 % by weight) R-134a.

When the optional R-134a is not included, a preferred refrigerant composition of the invention in terms of its suitability as a replacement for refrigerant R-502 is one comprising from 2 to 15 % by weight CO_2, from 28 to 70 % by weight R-125 and from 28 to 70 % by weight R-143a.

When the optional R-134a is not included, a particularly preferred refrigerant composition of the invention in terms of its suitability as a replacement for refrigerant R-502 is one comprising from 2 to 12 % by weight, more particularly from 2 to 10 % by weight, CO_2, from 38 to 60 % by weight, more particularly from 45 to 50 % by weight, R-125 and from 38 to 60 % by weight, more particularly from 45 to 50 % by weight, R-143a.

When the optional R-134a is included, a preferred refrigerant composition of the invention in terms of its suitability as a replacement for refrigerant R-502 is one comprising from 2 to 15 % by weight CO_2, from 27 to 70 % by weight R-125, from 27 to 70 % by weight R-143a and from 1 to 25 % by weight R-134a.

When the optional R-134a is included, a particularly preferred refrigerant composition of the invention in terms of its suitability as a replacement for refrigerant R-502 is one comprising from 2 to

15 % by weight, more particularly from 2 to 12 % by weight, CO_2, from 37 to 60 % by weight, more particularly from 35 to 45 % by weight, R-125, from 37 to 60 % by weight, more particularly from 43 to 53 % by weight, R-143a and from 1 to 10 % by weight, more particularly from 1 to 5 % by weight, R-134a.

The refrigerant composition of the invention may also be combined with one or more hydrocarbon compounds in an amount which is sufficient to allow the composition to transport a mineral oil or alkyl benzene type lubricant around a refrigeration circuit and return it to the compressor. In this way, inexpensive lubricants based on mineral oils or alkyl benzenes may be used to lubricate the compressor.

Suitable hydrocarbons for use with the refrigerant composition of the invention are those containing from 2 to 6 carbon atoms, with hydrocarbons containing from 3 to 5 carbon atoms being preferred. Propane and pentane are particularly preferred hydrocarbons, with pentane being especially preferred.

Where a hydrocarbon is combined with the refrigerant composition of the invention, it will preferably be present in an amount of from 1 to 10 % by weight on the total weight of the refrigerant composition.

The refrigerant composition of the invention may also be used in combination with the types of lubricants which have been specially developed for use with hydrofluorocarbon based refrigerants. Such lubricants include those comprising a polyoxyalkylene glycol base oil. Suitable polyoxyalkylene glycols include hydroxyl group initiated polyoxyalkylene glycols, e.g. ethylene and/or propylene oxide oligomers/polymers initiated on mono- or polyhydric alcohols such as methanol, butanol, pentaerythritol and glycerol. Such polyoxyalkylene glycols may also be end-capped with suitable terminal groups such as alkyl, e.g. methyl groups. Another class of lubricants which have been developed for use with hydrofluorocarbon based refrigerants and which may be used in combination with the present refrigerant compositions are those comprising a neopentyl polyol ester base oil derived from the reaction of at least one neopentyl polyol and at least one aliphatic carboxylic acid or an esterifiable derivative thereof. Suitable neopentyl polyols for the formation of

the ester base oil include pentaerythritol, polypentaerythritols such as di- and tripentaerythritol, trimethylol alkanes such as trimethylol ethane and trimethylol propane, and neopentyl glycol. The esters may be formed with linear and/or branched aliphatic carboxylic acids, such as linear and/or branched alkanoic acids. Preferred acids are selected from the C_{5-8}, particularly the C_{5-7}, linear alkanoic acids and the C_{5-10}, particularly the C_{5-9}, branched alkanoic acids. A minor proportion of an aliphatic polycarboxylic acid, e.g. an aliphatic dicarboxylic acid, may also be used in the synthesis of the ester in order to increase the viscosity thereof. Usually, the amount of the carboxylic acid(s) which is used in the synthesis will be sufficient to esterify all of the hydroxyl groups contained in the polyol, although residual hydroxyl functionality may be acceptable.

The zeotropic refrigerant composition of the present invention may be used to provide the desired cooling in heat transfer devices such as low temperature refrigeration systems by a method which involves condensing the refrigerant composition and thereafter evaporating it in a heat exchange relationship with a heat transfer fluid to be cooled. In particular, the refrigerant composition of the invention may be employed as a replacement for refrigerant R-502 in low temperature refrigeration applications.

The present invention is now illustrated but not limited with reference to the following example.

Example 1

The performance of five refrigerant compositions of the invention in a low temperature refrigeration cycle was investigated using standard refrigeration cycle analysis techniques in order to assess the suitability thereof as a replacement for R-502. The following refrigerant compositions were subjected to the cycle analysis:

(1) A composition comprising 2 % by weight CO_2, 43.1 % by weight R-125, 51 % by weight R-143a and 3.9 % by weight R-134a.
(2) A composition comprising 5 % by weight CO_2, 41.8 % by weight R-125, 49.4 % by weight R-143a and 3.8 % by weight R-134a.

(3) A composition comprising 10 % by weight CO_2, 39.6 % by weight R-125, 46.8 % by weight R-143a and 3.6 % by weight R-134a.

(4) A composition comprising 2 % by weight CO_2, 49 % by weight R-125 and 49 % by weight R-143a.

(5) A composition comprising 5 % by weight CO_2, 47.5 % by weight R-125 and 47.5 % by weight R-143a.

The following operating conditions were used in the cycle analysis.

Mean Evaporator Temperature:	-40°C
Mean Condenser Temperature:	40°C
Amount of Superheat:	10°C
Amount of Subcooling:	5°C
Isentropic Compressor Efficiency:	75 %
Cooling Duty:	1 kW

The results of analysing the performance of the five refrigerant compositions in a low temperature refrigeration cycle using these operating conditions are given in Table 1.

The performance parameters of the refrigerant compositions which are presented in Table 1, i.e. condenser pressure, evaporator pressure, discharge temperature, refrigeration capacity (by which is meant the cooling duty achieved per unit swept volume of the compressor), coefficient of performance (COP) (by which is meant the ratio of cooling duty (refrigeration effect) achieved to mechanical energy supplied to the compressor), and the glides in the evaporator and condenser (the temperature range over which the refrigerant composition boils in the evaporator and condenses in the condenser), are all art recognised parameters.

The performance of refrigerant R-502 under the same operating conditions is also shown in Table 1 by way of comparison.

It is apparent from Table 1 that the refrigerant compositions of the invention exhibited as good as or better refrigeration capacities than refrigerant R-502 and that the refrigeration capacity increased as the CO_2 content in the composition increased. It is also apparent from the results given in Table 1 that the performance of the refrigerant composition of the invention in a low temperature

refrigeration cycle is such that it could make an acceptable replacement for refrigerant R-502.

TABLE 1

Refrigerant % by weight	R502 100	CO_2/125/143a/134a 2/43.1/51/3.9	CO_2/125/143a/134a 5/41.8/49.4/3.8	CO_2/125/143a/134a 10/39.6/46.8/3.6	CO_2/125/143a 2/49/49	CO_2/125/143a 5/47.5/47.5
Evaporator Pressure (bar)	1.31	1.43	1.55	1.77	1.51	1.63
Condenser Pressure (bar)	16.82	19.77	22.01	25.63	20.32	22.6
Discharge Temperature (°C)	88.8	81.1	70.9	95.9	79.51	85.35
Coefficient of Performance (COP)	1.33	1.23	1.23	1.21	1.21	1.21
COP Relative to R502	1	0.92	0.92	0.91	0.91	0.91
Refrigeration Capacity (KJ/m^3)	667	671	741	847	685	752
Refrigeration Capacity Relative to R502	1	1	1.11	1.27	1.03	1.13
Evaporator Glide °C	0	1.2	2.1	3.7	0.6	1.5
Condenser Glide °C	0	3	6.3	9.8	2.7	5.9

Claims:

1. A non-azeotropic refrigerant composition comprising:
(A) carbon dioxide (CO_2);
(B) pentafluoroethane (R-125); and
(C) 1,1,1-trifluoroethane (R-143a).

2. A non-azeotropic refrigerant composition as claimed in claim 1 comprising from 1 to 20 % by weight CO_2, from 25 to 70 % by weight R-125, from 25 to 70 % by weight R-143a and from 0 to 25 % by weight 1,1,1,2-tetrafluoroethane (R-134a).

3. A non-azeotropic refrigerant composition as claimed in claim 1 comprising from 2 to 15 % by weight CO_2, from 28 to 70 % by weight R-125 and from 28 to 70 % by weight R-143a.

4. A non-azeotropic refrigerant composition as claimed in claim 3 comprising from 2 to 12 % by weight CO_2, from 38 to 60 % by weight R-125 and from 38 to 60 % by weight R-143a.

5. A non-azeotropic refrigerant composition as claimed in claim 4 comprising from 2 to 10 % by weight CO_2, from 45 to 50 % by weight R-125 and from 45 to 50 % by weight R-143a.

6. A non-azeotropic refrigerant composition as claimed in claim 1 which additionally comprises 1,1,1,2-tetrafluoroethane (R-134a).

7. A non-azeotropic refrigerant composition as claimed in claim 6 comprising from 1 to 20 % by weight CO_2, from 25 to 70 % by weight R-125, from 25 to 70 % by weight R-143a and from 1 to 25 % by weight R-134a.

8. A non-azeotropic refrigerant composition as claimed in claim 7 comprising from 2 to 15 % by weight CO_2, from 27 to 70 % by weight R-125, from 27 to 70 % by weight R-143a and from 1 to 25 % by weight R-134a.

9. A non-azeotropic refrigerant composition as claimed in claim 8 comprising from 2 to 15 % by weight CO_2, from 37 to 60 % by weight R-125, from 37 to 60 % by weight R-143a and from 1 to 10 % by weight R-134a.

10. A non-azeotropic refrigerant composition as claimed in claim 9 comprising from 2 to 12 % by weight CO_2, from 35 to 45 % by weight R-125, from 43 to 53 % by weight R-143a and from 1 to 5 % by weight R-134a.

11. A non-azeotropic refrigerant composition as claimed in any one of claims 1 to 10 which additionally comprises at least one hydrocarbon.

12. A non-azeotropic refrigerant composition as claimed in claim 11, wherein the at least one hydrocarbon contains from 2 to 6 carbon atoms.

13. A non-azeotropic refrigerant composition as claimed in claim 12, wherein the at least one hydrocarbon is selected from propane and pentane.

14. A non-azeotropic refrigerant composition as claimed in any one of claims 11 to 13, wherein the hydrocarbon is present in an amount of from 1 to 10 % by weight on the total weight of the refrigerant composition.

15. A heat transfer device containing a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 14.

16. A low temperature refrigeration system containing a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 14.

17. A method for providing cooling which comprises condensing a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 14 and thereafter evaporating it in a heat exchange relationship with a heat transfer fluid to be cooled.

18. The use of a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 14 as a replacement for refrigerant R-502 in low temperature refrigeration applications.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/01955

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,41 16 274 (FORSCHUNGSZENTRUM FÜR KÄLTETECHNIK UND WÄRMEPUMPEN) 19 November 1992 see column 2, line 63 - line 67 see claims 1-5 ---	1,15-18
A	WO,A,92 16597 (ALLIED-SIGNAL) 1 October 1992 see claims 1,4-6,10 ---	1,16,17
A	EP,A,0 583 179 (ELF ATOCHEM) 16 February 1994 see the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 1996	11. 12. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Puetz, C

INTERNATIONAL SEARCH REPORT

Inten. ...nal Application No
PCT/GB 96/01955

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-4116274	19-11-92	NONE	
WO-A-9216597	01-10-92	AU-A- 1642192	21-10-92
		CN-A- 1065085	07-10-92
		DE-D- 69210994	27-06-96
		DE-T- 69210994	10-10-96
		EP-A- 0576550	05-01-94
		ES-T- 2087536	16-07-96
		JP-T- 6506015	07-07-94
EP-A-583179	16-02-94	FR-A- 2694764	18-02-94
		AU-A- 4457893	17-02-94
		CA-A- 2100693	13-02-94
		FI-A- 933541	13-02-94
		JP-A- 6172227	21-06-94
		NO-A- 932451	14-02-94
		ZA-A- 9305843	10-03-94